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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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16. März 1999

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Rosin Amine Anti-Fouling Agents**Field of invention**

5 The invention relates to new and known compounds as well as methods for preventing the attachment of aquatic organisms to surfaces which are submerged for extensive periods of time in water. More particularly, this invention relates to the protection of submerged surfaces with new isonitrile, formamide, isocyanate and isothiocyanate anti-fouling agents.

10

Background of the invention

15 The ever recurring growth of fouling organisms on underwater structures such as ships, docks, piers, pilings, fishnets, heat exchangers, dams, piping structures, intake screens, cooling towers and the like is a costly and hazardous problem in both marine and freshwater endeavors. The presence of fouling organisms such as barnacles, zebra mussels, algae, diatoms, hydroids, bryozoa, ascidians, tubeworms, Asiatic clams and the like causes economic damage in various ways: for example, attachment to the hulls of ships reduces fuel efficiency and causes loss of profitable sailing time because of the need to clean the hulls. Similarly, the attachment of these organisms to cooling water equipment decreases heat conductivity which eventually reduces or block the cooling power of the equipment and drives up cost.

20

A variety of agents useful for controlling fouling organisms in fresh water or sea water have been used to prevent the attachment and overgrowth of these organisms.

25 A common method of controlling the presence or attachment of fouling organisms is to coat or permeate the underwater structure with a composition which comprises mixtures of toxic compounds such as tri-n-butyl tin or copper compounds. Anti-fouling agents in the form of a paint can contain up to 60% by weight of the active ingredients and can be used to paint surfaces such as the hull of ships. The paint prevents attachment and growth of fouling organisms by continuously releasing anti-fouling agents underwater. The disadvantage of many of the present anti-fouling

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agents is that they are persitant in the environment, are often acutely toxic and degrade too slowly in aquatic environments and are, therefore, ecologically harmful. Hazardous anti-fouling agents can eventually bioaccumulate and enter the food chain and therefore represent a threat to marine and human life.

5

For example, it is well established that heavy metal compounds, especially organotin compounds that are widely used as anti-fouling agents, accumulate in mussels.

10

It is an object of this invention to provide an environmentally and ecologically sound method of combatting or controlling marine and freshwater fouling organisms.

It is another object of this invention to provide an effective method for protecting aquatic structures against fouling by marine or freshwater fouling organisms.

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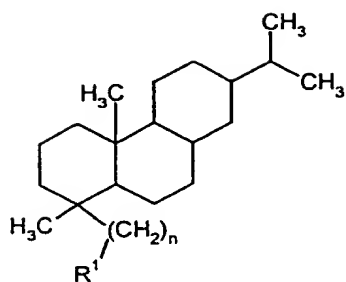
It is a further object of this invention to provide antifoulant compositions which comprises certain derivatives of rosin compounds as the active agents.

Summary of the Invention

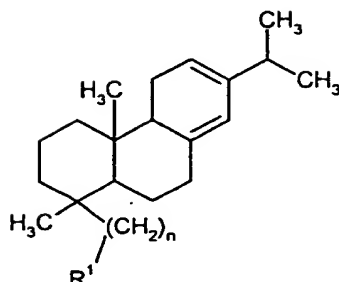
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The present invention provides new and known compounds and a method to prevent settlement on surfaces by marine or freshwater fouling organism which comprises contacting said organism or the locus thereof with an anti-fouling-effective amount of at least one compound of formula I1-I13

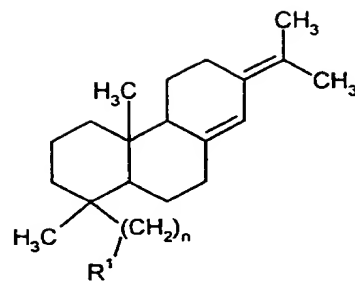
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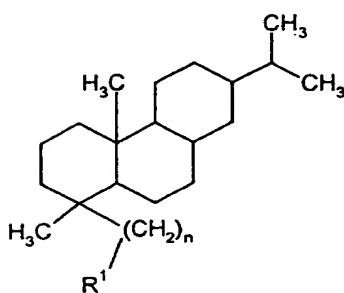
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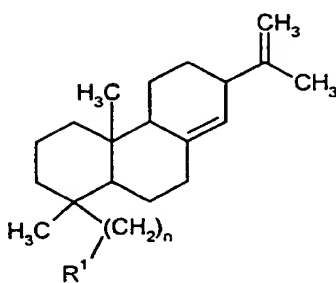
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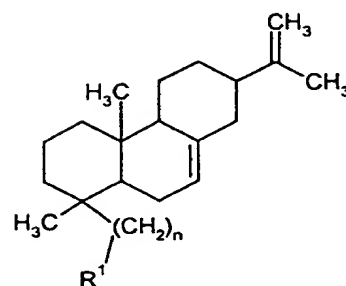
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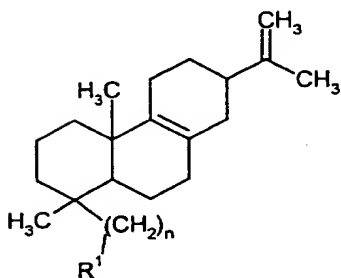
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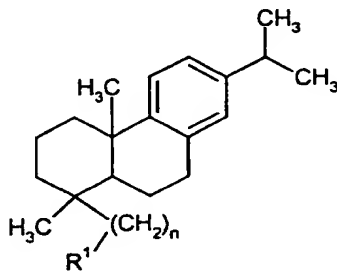
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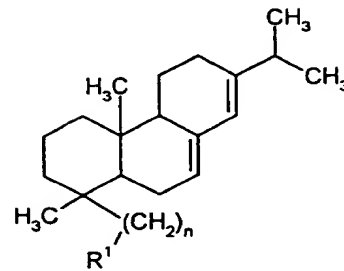
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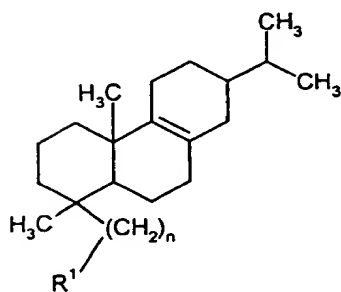
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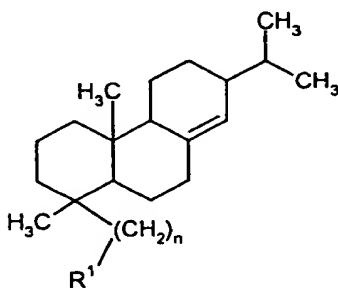
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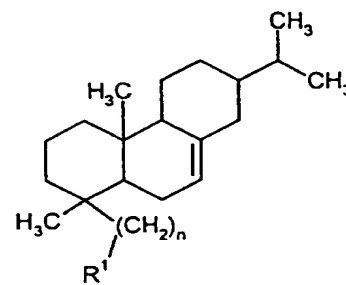
I9



I10



I11



I13

formula I1 -I13

- 4 -

wherein

- 5 R^1 represents NR^2R^3 wherein
 R^2 represents a hydrogen atom, C1 - C8-alkyl and
 R^3 represents $C=OR^4$ wherein
 R^4 represents a hydrogen atom or one of the groups OR^5 or NHR^5 wherein
 R^5 designates C1 - C8-alkyl or aryl, each optionally substituted by
 halogen; or
- 10 R^1 represents $N=CR^6R^7$ wherein
 R^6 represents a hydrogen atom, C1 - C6-alkyl or aryl, and
 R^7 represents C1 - C6-alkyl or aryl, each optionally substituted by
 halogen; or
- 15 R^1 represents an isonitrile, isocyanate, isothiocyanate or a guanidino group; and
 n represents 0 or 1.

In the specification and claims the term:

halogen has the meaning of Cl, Br, I or F;

- 20 alkyl has the meaning of straight-chain or branched alkyl with 1 to 8, preferably 1 to
 4 carbon atoms;

aryl has the meaning of aromatic, mono- or polycyclic hydrocarbon rings such as for
example and preferred: naphthyl, anthranyl, phenanthryl, especially phenyl.

- 25 Preferred are compounds of formula I1 - I13 wherein

- R^1 represents NR^2R^3 wherein
 R^2 represents a hydrogen atom or C1 - C4-alkyl and
 R^3 represents $C=OR^4$ wherein
30 R^4 represents a hydrogen atom or one of the groups OR^5 or NHR^5
 wherein

- 5 -

R⁵ represents C1 - C4-alkyl or aryl, each optionally substituted by halogen; or

R¹ represents N=CR⁶R⁷ wherein

5 R⁶ represents a hydrogen atom, methyl or optionally halogen substituted aryl, and

R⁷ represents C1 - C4-alkyl or optionally halogen substituted aryl; or

R¹ represents an isonitrile, isocyanate, isothiocyanate or guanidino moiety.

10

Especially preferred are compounds of formula I1 - I13 wherein

R¹ represents NR²R³ wherein

R² represents a hydrogen atom and

R³ represents C=OR⁴ wherein

15 R⁴ represents a hydrogen atom.

Especially preferred are also compounds of formula I1 - I13 wherein

R¹ represents NR²R³ wherein

R² represents a hydrogen atom and

20 R³ represents C=OR⁴ wherein

R⁴ represents OR⁵ or NHR⁵ wherein

R⁵ represents methyl, ethyl, n- or i-propyl or n-,s-,i- or t-butyl, or phenyl which is optionally substituted by halogen.

25 Especially preferred are also compounds of formula I1 - I13 wherein

R¹ represents N=CR⁶R⁷ wherein

R⁶ represents methyl, ethyl, n- or i-propyl, n-,s-,i- or t-butyl, or preferred a hydrogen atom or and

R⁷ represents methyl, ethyl, n- or i-propyl, n-,s-,i- or t-butyl or phenyl.

30

Especially preferred are also compounds of formula I1 - I13 wherein

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R^1 represents an isonitrile, isocyanate, isothiocyanate or guanidino moiety.

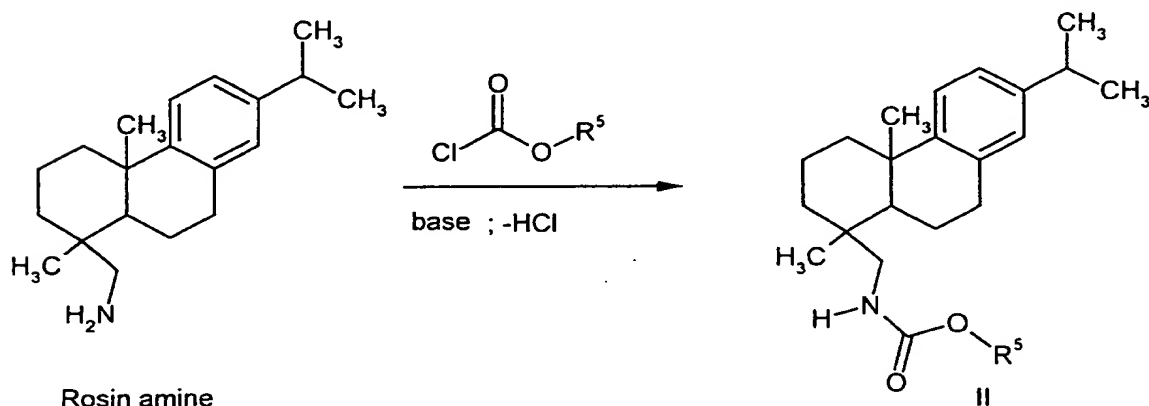
Preferred are compounds wherein n represents 1.

5 Preferred are compounds of the formula I8

The aforementioned compounds are accessible by standard procedures of organic chemistry which can be adopted to the Rosin moiety. The starting Rosin derived from Tall Oil, Gum or Wood is commercially available; for example Rosin amine as
10 Hercules® Amine D. An overview on the different isomers of abietic acid as well as their preparation is given by Gang-Fung Chen in *Progress in Organic Coatings* 20, 1992, 139-167. In the following general schemes the synthesis of the different Rosin amine derivatives is outlined. For reasons of simplification, the synthesis routes are outlined for substructure I8 with $n = 1$. The reaction sequences can be adopted easily
15 to the other pure isomers and rosin oxidation/reduction products and also to mixtures of them.

Scheme 1

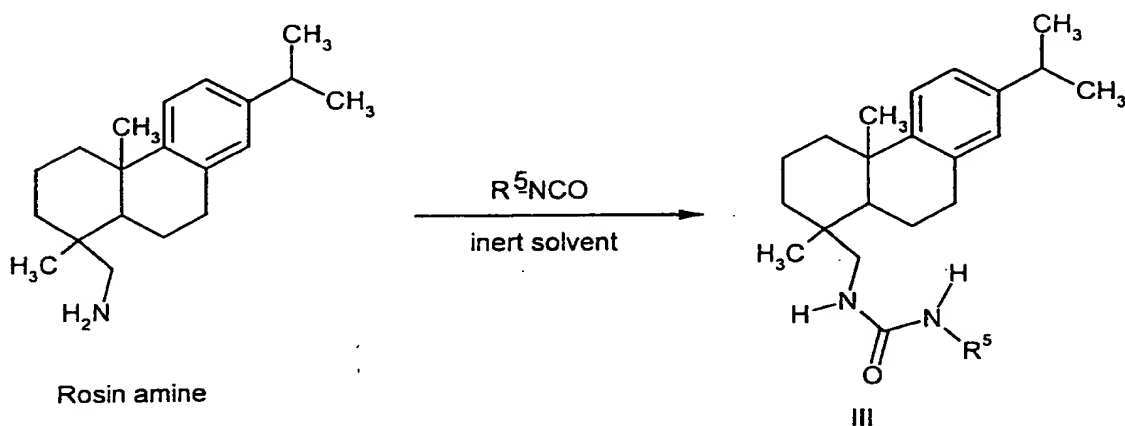
Compounds of formula I8 are accessible via acylation of Rosin amine with a chloro-
20 formic-ester in an inert solvent with a base as HCl acceptor (see: Houben-Weyl Vol.8, 1952, 137-140; ibid. Vol.11/2, 1958, 27-37).



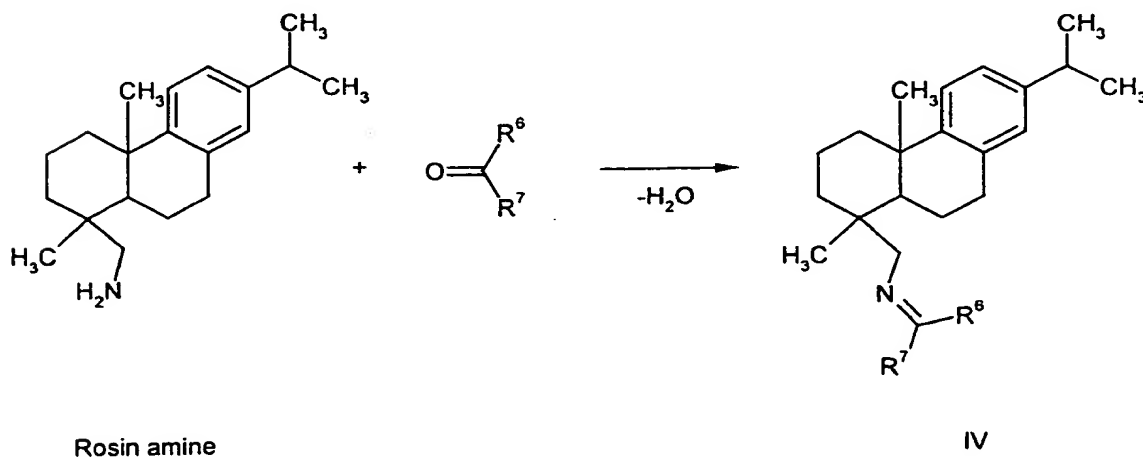
- 7 -

Scheme 2

Ureas of formula III can be synthesized by reacting Rosin amine with an isocyanate in an inert solvent (benzene, toluene, hydrocarbons etc.); see: Houben-Weyl Vol. E4, 1983, 352-357 or alternatively via reaction of Rosin isocyanate (s. below) with an aliphatic or aromatic amine.

10 **Scheme 3**

Schiff-bases of Rosin amine are accessible via condensation of Rosin amine with an aldehyde or keton (Houben-Weyl Vol. 11/2, 1958, 74-85).



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The synthesis of Rosin isocyanide has been published (T. Ohsawa et al., Tetrahedron Lett., 1989, 845-846).

5 Rosin isothiocyanate (CAS-Nr.: 115 269-93-7) can be synthesized from Rosin amine through reaction with thiophosgene (see analogous sequence with phosgene: Ozaki, Chem Rev. 72, 457-460), or alternatively with a thiophosgene substitute, namely thiocarbonyl-diimidazole (see example 3).

10 The preparation of Rosin isocyanate has been described (E.Corey et al., Tetrahedron Lett. 1981, 299-302).

15 In the case of compounds of formula 1 with $n = 0$, the required starting material Dehydroabietan-1-yl-amine can be obtained according to Stockel et al., Can.J.Chem. 1963, 834-836.

The synthesis of Dehydroabietan-1-yl-isocyanate is described in Chem.Pharm.Bull. 1985, 1472-1487.

20 All other derivatives (formula I, $n=0$) can be synthesized in analogous manner as described for Rosin amine.

Detailed Description of the Preferred Embodiment

A fouling organism which may be combatted or controlled by the method of the invention can be any marine or freshwater organism which can attach to an inner or
25 outer surface of a structure which is submerged or in continual contact with water. Exemplary organisms include algae, including members of the phyla Chlorophyta, Phaeophyta and Rhodophyta; tunicates, including members of the class Ascidiacea such as *Ciona intestinalis*, *Diplosoma listerianum* and *Botryllus sclosseri*, and members of the class Hydrozoa including *Clava squamata*, *Hydractinia echinata*,
30 *Obelia geniculata* and *Tubularia larynx*;

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Bivalves including *Mytilus edulis*, *Cassostrea virginica*, *Ostrea edulis*, *ostrea chilensis*, *Lasaea rubra* and members of the family Dreissenidae (or zebra mussels) and members of the family Corbuculidae (or Asiatic clams), bryozoans including *Electra pilosa*, *Conopeum reticulatum*, *Bugula neritina* and *Bowerbankia gracilis*;

5

Polychaete worms including *Hydroides norvegica*, *Pomatoceros triqueter*, *Mercierella enigmata* and *Spirorbis spp.*;

10

Sponges and members of the class Cirripedia (barnacles) such as *Balanus amphitrite*, *Lepas anatifera*, *Balanus balanus*, *Balanus balanoides*, *Balanus hameri*, *Balanus creatus*, *Balanus improvisus*, *Balanus galeatus*, *Balanus eburneus*, *Elminius modestus*, *Balanus tulipiformis* and *Balanus perforatus*.

15

Organisms of the genus *Balanus* are frequent foulers of aquatic structures. Specific fouling organisms to which this invention is especially directed include barnacles, zebra mussels, algae, diatoms, hydroids, bryozoa, ascidians, tube worms and asiatic clams, but also the bacterial slime.

20

Among the aquatic structures which may be protected by the method of invention are any submerged or partially submerged structure, either mobile or stationary, such as a fishnet, boat, ship, piling, cooling tower, pipeline, standpipe, heat exchanger, dam, intake screen or the like.

25

In actual practice compound of formula I1 - I13 may be brought into contact with a fouling organism by:

30

- coating the aquatic structure to be protected with an antifouling-effective amount of said Rosin Amine derivative such that the antifouling compound is released at the to be protected surface area into the aquatic environment immediately.

- 10 -

- including an antifouling-effective amount of the Rosin Amine Derivative within material formed into an aquatic structure which then releases said compound,
- 5 ■ releasing an antifouling-effective amount of said compound directly into the aquatic environment surrounding the structure to be protected,
- or any other method wherein the Rosin Amine Derivative comes in contact with the fouling organism.

10

The amount of Rosin Amine Derivative to be used in the method of invention will vary according to the specific compound used, the identity of the fouling organism to be controlled, degree of fouling pressure of the surrounding aquatic environment, the water temperature, the mode of contact and the like.

15

The Rosinamine derivatives can be used as individual active compounds or else in combination with active compounds usually employed in the anti-fouling sector. These can preferably be heavy metals, such as Cu, or heavy metal compounds, such as, for example, bis(trialkyltin) sulphides, tri-n-butyl laurate, tri-n-butyl chloride, 20 copper(I) oxide, triethyltin chloride, tri-n-butyl(2-phenyl-4-chlorophenoxy)-tin, tributyltin oxide, molybdenum disulfide, antimony oxide, polymeric butyl titanate, phenyl-(bispyridine)-bismuth chloride, tri-n-butyltin fluoride, manganese ethylene-bisdithiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate, the zinc salt or copper salt of 2-pyridinethiol-1-oxide, bisdimethyldithiocarbamoyl- 25 zinc ethylenebisdithiocarbamate, zinc oxide, copper(I) ethylene-bis-dithiocarbamate, copper thiocyanate, copper naphthenate and tributyltin halides.

25

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The action spectrum of the rosinamine derivatives is extended further or particular effects are achieved by these combinations of active compounds. Synergistic effects are obtained in many cases. The synergistic effect manifests itself particularly clearly if the active compound combinations are present in certain weight ratios. However,

- 11 -

the weight ratios of the active compounds in the active compound combinations can vary within a relatively wide range.

Preferred combination partners for the rosinamine derivatives are algicides, such as diuron, dichlorophen, endothal, fentin acetate or quinoclamine, molluscicides, such as fentin acetate, metaldehyde, methiocarb, niclosamide, thiodicarb and trimethacarb, fungicides, such as dichlofluanid, tolylfluanid, iodopropargyl butylcarbamate, fluorfolpet and azoles, such as propiconazole, metconazole, cyproconazole and tebuconazole or conventional antifouling active compounds, such as 2-(N,N-dimethylthiocarbamoylthio)-5-nitrothiazyl, tetrabutyl-distannoxane, 2-tert-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, 2,4,5,6-tetrachloroisophthalodinitril, tetramethylthiuram disulphide, 2,4,6-trichlorophenylmaleimide, 2,3,5,6-tetrachloro-4-(methylsulphonyl)-pyridine, diiodomethylparatryl sulphone, thiabendazol, tetraphenyl-boron-pyridin salt, and the copper and sodium salt of 2-pyridinethiol-1-oxide.

The anti-fouling composition preferably comprises the rosinamine derivatives in concentrations of 0.5 to 60% by weight, preferably between 1 to 25% by weight.

Compositions of the invention comprise an aquatically acceptable inert carrier and an antifouling-effective amount of a Rosin Amine Derivative of formula I. For application onto structural surfaces, preferred compositions of the invention include a film-forming component such as a polymer resin solution. Exemplary polymer resins include unsaturated polyester resins formed from: a) unsaturated acids or anhydrides, such as maleic anhydride, fumaric acid, itaconic acid and the like; b) saturated acids or anhydrides, such as phthalic anhydride, isophthalic anhydride, terephthalic anhydride, tetrahydrophthalic anhydride, tetrahalophthalic anhydride, adipic acid, suberic acid, and the like; c) glycols, such as ethylene glycol, and the like; d) vinyl monomers, such as styrene, vinyl toluene, chlorostyrene, bromostyrene, acrylates like methylmethacrylate, ethylene glycol dimethacrylate and the like. Other suitable

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resins include vinyl ester-, vinyl acetate-, and vinyl chloride-based resins, elastomeric components, vulcanized rubbers, rosins, metalresinates and urethane-based resins.

For further description of components common in antifouling paints see Ungerer in
5 Chem.Ind. 1985, 37, 730 - 732 and Williams in Antifouling Marine Coatings,
Noyes, Park Ridge, 1973.

Example 1

N-Formyl-rosinamine (1)

10 The starting material Rosinamine (Hercules® Amine D) is a mixture of primary amines derived from modified Rosin. It is described as dehydroabietylamine of technical grade and was used in the following syntheses without further purification.

15 To a solution of Rosin amine in ethyl acetate 5 equiv. of ethyl formate are added at room temperature under continuous stirring. After 16h at rt, the solvent is evaporated to dryness and the residue is filtered through a short column of silica gel to furnish N-formyl rosin amine under the form of a compact resin (yield: 86%).

Characterisation: visqueous oil; ¹H-NMR, δ(ppm): 7.94-8.23(1H); 7.15 (1H); 6.99 (1H); 6.89 (1H); 5.46 (1H); 2.76-3.27 (5H); 1.22 (6H); 1.21 (3H); 0.95 (3H).

20

Example 2

Rosin isocyanide (2)

Diisopropylamine (2.7 equiv.) and phosphorous oxychloride (1.1equiv.) were successively added dropwise to a stirred solution of N-formyl rosinamine in
25 dichloromethane at 0°C under an atmosphere of dry nitrogen. After 1h at 0°C, a 20% solution of sodium carbonate was added and the reaction mixture was allowed to reach room temperature for 1h. 20% sodium carbonate and water were added, extraction of the aqueous phase with dichloromethane followed by filtration of the residue through a column of silica gel furnished Rosin isocyanide as a colourless oil
30 (yield: 85%).

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Characterisation: visqueous oil; ^1H NMR, $\delta(\text{ppm})$: 7.16 (1H); 7.00 (1H); 6.88 (1H); 2.76-3.34 (5H); 1.22 (6H); 1.21 (3H); 0.98 (3H).

Example 3

5 Rosin isothiocyanate (3)

A solution of thiocarbonyl diimidazole (1.5equiv.) in dichloromethane was added to a stirred solution of Rosinamine in dichloromethane at 0°C under an atmosphere of dry nitrogen. After the addition was complete, the reaction mixture was heated at 45°C during 16h. The solvent was evaporated and the solid residue filtered through a
10 column of silica gel to furnish Rosinisothiocyanate as an oil (yield: 87%).

Characterisation: oil; ^1H -NMR, $\delta(\text{ppm})$: 7.16 (1H); 6.99 (1H); 6.89 (1H); 3.37 (2H); 2.90 (2H); 2.82 (1H); 1.22 (6H); 1.21 (3H); 0.96 (3H).

Evaluation of Marine Antifouling Activity of Test Compounds

- 15 The rate of settlement of laboratory reared cyprid larvae of the barnacle *Balanus amphitrite* was determined for testing the activity of candidate anti-fouling compounds.

Settlement Assay

- 20 Tests are carried out in four replicates in sterile polystyrene multi well plates. Between 25 and 40 cyprid larvae are injected in the dishes containing either 2ml of test solution (see below), solvent control or a positive control (Dichloro-n-octyl-isothiazolinone).

- 25 Dishes are incubated for 24h at a temperature of $27^\circ\text{C} \pm 2$. After incubation the cyprids are screened for signs of toxicity. Larvae are classified in three categories: A) alive and swimming; B) alive but not active; C) dead. The test is terminated by addition of a drop of 20% formaldehyde and the numbers of settled and non-settled larvae are counted.

30

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Settlement is evaluated as follows: 1) Non settled: not attached free swimming cyprids; 2) settled cyprids: attached, but not metamorphosed cyprids; 3) barnacles: attached juvenile barnacles.

- 5 Categories 2 and 3 are considered to be settled. Percentage settlement in test solution is compared with controls. Estimates of the *median effect concentration* (EC-50) after 50 hrs. are calculated using the Spearman-Kärber method.

- 10 All seawater used is of natural origin and filtered unto 0.2 micron. Stock solutions of test compounds are prepared by dissolving an amount of test substance in a suitable solvent and subsequent addition of seawater.

- 15 The stock solutions are used to prepare several dilution series in seawater. Controls are made of seawater, or, if appropriate, in a mixture of seawater and solvent. The solvent concentration in the controls is equal to the highest concentration in the test solution. As an internal standard (positive control) a concentration range of 0 to 5ppm dichloro-n-octylisothiazolinone will is included in each test.

Test Results

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Compound	EC50 for settlement inhibition in ppm
1	2.6
2	0.12
reference*	0.37

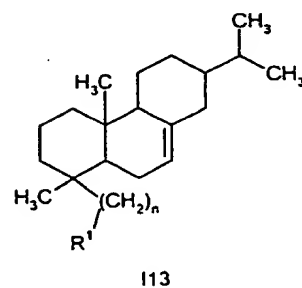
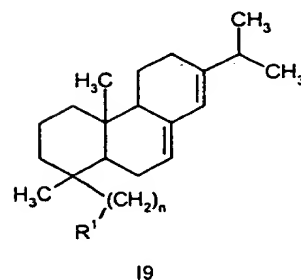
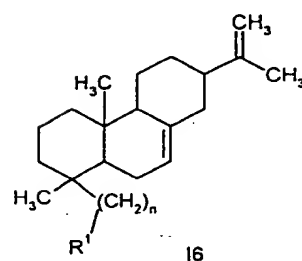
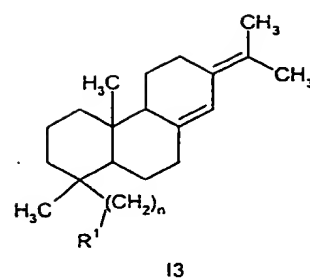
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* = 4,5-dichloro-n-octylisothiazolinone

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16. März 1999

1. Compounds of the formula I



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R¹ represents NR²R³ wherein

R² represents a hydrogen atom, C1 - C8-alkyl and

R³ represents C=OR⁴ wherein

R⁴ represents a hydrogen atom or one of the groups OR⁵ or NHR⁵ wherein

R⁵ designates C1 - C8alkyl or aryl, each optionally substituted by halogen; or

R¹ represents N=CR⁶R⁷ wherein

R⁶ represents a hydrogen atom, C1 - C6-alkyl or aryl, and

R⁷ represents C1 - C6-alkyl or aryl, each optionally substituted by halogen; or

R¹ represents an isonitril, isocyanate, isothiocyanate or guanidino group; and

n represents 0 or 1.

2. Compounds of the formula I according to claim 1, wherein

R¹ represents NR²R³ wherein

R² represents a hydrogen atom or C1 - C4-alkyl and

R³ represents C=OR⁴ wherein

R⁴ represents a hydrogen atom or one of the groups OR⁵ or NHR⁵ wherein

R⁵ represents C1 - C4-alkyl or aryl, each optionally substituted by halogen; or

R¹ represents N=CR⁶R⁷ wherein

R⁶ represents a hydrogen atom, methyl or optionally halogen substituted aryl, and

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R⁷ represents C1 - C4-alkyl or optionally halogen substituted aryl;
or

R¹ represents an isonitrile, isocyanate, isothiocyanate or guanidino moiety.

3. Compounds of the formula I according to claim 1, wherein

R¹ represents NR²R³ wherein

R² represents a hydrogen atom and

R³ represents C=OR⁴ wherein

R⁴ represents a hydrogen atom.

4. Method for controlling or combatting a marine or freshwater fouling organism which comprises contacting said organism or the locus thereof with an anti-fouling-effective amount of at least one compound of formula I as defined in claim 1.

5. Agents, characterized in that they comprise an antifouling-effective amount of at least one compound of formula I as defined in claim 1 and an aquatically acceptable inert carrier.

6. Use of compounds of formula I or agents as defined in claims 1 and 3 to control and combat marine and/or freshwater fouling organism.

7. Process for the preparation of anti-fouling agents, characterized in that compounds of formula I as defined in claim 1 are mixed with an aquatically acceptable inert carrier.

Rosin Amine Anti-Fouling Agents**A b s t r a c t**

The invention relates to new and known compounds as well as methods for preventing the attachment of aquatic organisms to surfaces which are submerged for extensive periods of time in water. More particularly, this invention relates to the protection of submerged surfaces with new isonitrile, formamide, isocyanate and isothiocyanate anti-fouling agents.

